

A direct pathway for sticking/desorption of H_2 on $\text{Si}(100)$

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Abstract

The energetics of H_2 interacting with the $\text{Si}(100)$ surface is studied by means of *ab initio* total energy calculations within the framework of density functional theory. We find a direct desorption pathway from the mono-hydride phase which is compatible with experimental activation energies and demonstrate the importance of substrate relaxation for this process. Both the transition state configuration and barrier height depend crucially on the degree of buckling of the Si dimers on the $\text{Si}(100)$ surface. The adsorption barrier height on the clean surface is governed by the buckling via its influence on the surface electronic structure. We discuss the consequences of this coupling for adsorption experiments and the relation between adsorption and desorption.

1 Introduction

In the last years, the $\text{H}/\text{Si}(100)$ system has gained a growing attention experimentally as well as theoretically. Apart from its technological importance, this system is interesting because it is a simple example for the interplay between hydrogen adsorption and the reconstruction of a semiconductor surface. Consequently, it has become one of the most intensively studied adsorption system on a semiconductor surface. The rich experimental material available for H_2 desorption from $\text{Si}(100)$ has raised a number of questions, and even quite fundamental issues are subject to controversy. The remarkable discovery that this reaction obeys first order kinetics [1, 2] has started a lively debate over the desorption mechanism. Among the suggested mechanisms, which included irreversible excitation of hydrogen atoms into a band-like state [1], desorption mediated by surface defects [3, 4, 5], and concerted desorption from a “pre-paired” configuration [6], the last one has gained most support from experimental observations. While earlier experiments showed a considerable spread in the

activation energy for desorption, covering values of 1.95 eV [7], 2.17 eV [1], 2.51 eV and 2.86 eV [8], more recent experiments agree in an activation energy close to 2.5 eV [2, 9] for well-prepared, ordered surfaces.

The energy distribution within the reaction product H_2 has been studied extensively in a number of experiments. Roughly 1% and 0.2% of the H_2 molecules desorbing from the mono-hydride and di-hydride phase, respectively, are in the first vibrationally excited state. In both cases this is a factor of 20 more than one would expect for molecules in equilibrium with the surface. On the other hand, the rotational temperature of the molecules is lower than the surface temperature [10]. From these findings and measurements of the translational energy it has been concluded that the total energy of the desorbing molecules shows no evidence for a substantial barrier for adsorption [11]. On the other hand, sticking of H_2 on Si(100) could not be detected until recently. This has raised speculations about a high barrier towards dissociative adsorption, which seems to be difficult to reconcile with the desorption data. Very recent experiments, however, show that some sticking is possible at elevated surface temperatures. Kolasinski, Nessler, Bornscheuer and Hasselbrink have shown that sticking from a molecular beam is activated with respect to the total energy of the adsorbing molecules, but also with respect to the substrate temperature [12]. Bratu and Höfer found an even stronger activation of sticking with surface temperature for a thermal gas of both H_2 and D_2 [13]. These findings point towards the importance of the substrate degrees of freedom for a possible solution of the barrier puzzle. Structural considerations give further support to this picture: For the clean Si(100) surface the existence of the ‘buckled dimer’ reconstruction has been established experimentally [14] as well as theoretically [15]. In the (2x1)-phase of the H-covered surface, however, the dimers are symmetric, suggesting that considerable rearrangement of the substrate atoms must be involved in the adsorption process.

Earlier theoretical efforts have concentrated on total energy calculations for Si clusters based on ab initio Hartree-Fock/CI methods [3, 4, 16]. The calculations of Wu, Ionova and Carter showed that the barrier height is sensitive to substrate relaxation [3]. Under the assumption that H_2 desorption proceeds in a single step, part of the results [3, 4] were at variance with the observed thermal activation energies. Therefore, these two groups argued in favor of a two-step desorption mechanism via SiH_2 groups formed at defect sites. Such a mechanism, however, is compatible with first-order reaction kinetics only if diffusion of hydrogen atoms on the surface is the rate-limiting step, which is very unlikely in the light of recent modeling of the diffusion process [17, 18]. The agreement in the desorption rate and the reproducibility of the activation energy in recent experiments also argues against the role of defects. Recently substantial progress has been made towards a better understanding of the energetics of H_2 desorption. By comparing two cluster calculations, Nachtigall and coworkers [19] showed that a description of exchange and correlation based on non-local density functional theory gives a Si-H bond energy in fair agreement with, though systematically lower than conventional quantum chemistry methods.

The heat of chemisorption derived from their results is compatible with the observations, although their cluster calculations give a too high desorption barrier for a direct desorption mechanism to work [5]. However, recent slab calculations [20, 21, 22] agree in a fairly low adsorption barrier, and desorption through this transition state gives a barrier in good agreement with the experimental values. Therefore, we see no further need to invoke a defect-mediated mechanism for desorption on energetic grounds.

In this paper, we present *ab initio* calculations for the energetics of H_2 adsorption on a laterally infinite slab. A preliminary account of the present calculations was given in ref.[20]. We discuss in detail the coupling of adsorption to the substrate, making advantage of the fact that the reconstruction of the clean Si(100) is well described in our approach. We discuss the consequences of our findings for the dynamics of desorption and adsorption and relate our results to the experimental data.

2 Calculations

We performed total energy pseudopotential calculations within a basis set consisting of plane waves. In this approach Hellmann-Feynman forces on the ions can easily be derived. These forces are used to relax the ions and to determine the stable structures. Unless otherwise stated, the slab consisted of a periodically repeated 2x1 unit cell in the lateral directions, build up from 6 layers of Si atoms in the z direction, separated by a vacuum region corresponding to another 6 layers. Test calculations were performed for an 8 layer slab as well. Both of these slabs contained a glide plane in the middle, with hydrogen adsorbing on both sides. To demonstrate that our calculations are reasonably converged with respect to layer thickness, we also tried an asymmetric configuration with the adsorbing H_2 on one side of the slab, the dangling bonds on the other side being saturated with (static) di-hydride units. Results of these convergence tests are collected in table 1.

Our approach is based on the density functional theory. For the exchange and correlation energies we can employ either the local density approximation (LDA) [23] or the generalized gradient approximation (GGA) [24]. For systems with H atoms in different chemical environments, such as free H_2 compared to H adsorbed on surfaces, GGA calculations have been shown to give reliable results, whereas the LDA calculations are at variance with experimental data [25, 26, 27]. Similar observations have been reported for CO adsorption on metal surfaces [28, ?]. This leads us to the conclusion that the GGA is the method of choice for our system. We have calculated electronic densities self-consistently in the LDA, which serve as an input for the non-local exchange-correlation expression of the GGA. This approximation has been shown to work accurately for a number of systems [25].

The electronic ground state of the system is found by conjugate gradient minimizations of the total energy [30], interlaced by subspace rotations as suggested by Gillan [31]. Since the unreconstructed Si(100) surface is metallic, it is necessary to treat par-

tially occupied bands. In order to stabilize the process of determining the electronic ground state, we introduced a finite electronic temperature of $k_B T = 10\text{meV}$ as a technical parameter, which allows us to obtain occupation numbers from a smooth Fermi distribution. The smallness of the smearing assures that the semiconducting character of bulk silicon is unaffected. Quoted electronic energies have been extrapolated to zero electronic temperature.

To model the Si atoms we employ the sp-nonlocal pseudopotential of Bachelet, Hamann and Schlüter [32], which was brought to the Kleinmann-Bylander form [33]. Hydrogen is described by the Coulomb potential of a proton. The numbers quoted in this paper were obtained using a plane wave basis set with kinetic energies up to 30 Ry. This basis set quality is mainly dictated by the requirement to represent accurately the electronic wavefunctions and binding energies of hydrogen. Tests were done also at 40 Ry (see table 1). K-space sampling was performed with a density corresponding to 32 k-points in the first surface Brillouin zone (SBZ) of the 2x1 unit cell. The symmetry of the slab was exploited to reduce the number of independent k-points actually used in the calculations [34]. Computing the bulk silicon properties under these conditions, we obtained a bulk modulus of 0.97 MBar and a lattice constant of 5.394 Å, which was used throughout the further calculations.

During the search for the transition state both the hydrogen atoms and the Si atoms of the two outer layers of the slab were allowed to move within the plane containing the dimer bond. At least two inner layers of the slab were kept static. Since the transition state is a local maximum in the direction of the reaction coordinate, it is necessary to impose some constraint (e.g. fixed H-H distance) to prevent the system from sliding down the reactant or product valley. Calculations were repeated with different constraints until the transition state could be pinned down. The reaction path was then determined by unconstrained steepest descent minimization on both sides of the saddle point. For the sake of computational feasibility this part of the calculation was performed with a 10 Ry basis set cut-off and a sampling quality of 8 k-points in the 2x1 SBZ only. However, we stress that all energies quoted and plotted in this paper are based on the more converged parameter set (30Ryd and 32 k-points).

3 Results

3.1 Surface Structure

As a starting point we determined the stable structures of the H/Si(100) system by relaxing the adsorbate and the two Si layers beneath it. For the mono-hydride in the (2x1) phase we obtain an equilibrium geometry with a distance of 2.44Å in the Si dimer. The Si-H bond is 1.51Å long and forms an angle of 112.3° with the Si dimer axis. The clean surface consists of buckled Si dimers with a bond length of 2.28Å. In the following, all energies refer to the sum of the energy of the H₂ and the

clean, buckled surface. On this scale, the hydrogenated Si dimer has a total energy of -2.14eV , which corresponds to a mean Si-H bond strength of 3.45eV . The isomeric structure with a di-hydride at one Si atom and two dangling bonds at the other is metastable and has an energy of -0.45eV on this scale. The difference is mainly due to the absence of the Si dimer bond, while the Si-H bond strength only decreases slightly to 3.32eV . For the length of this bond we obtained 1.55\AA .

In the following we restrict ourselves to the 2×1 mono-hydride phase, which is the ground state of the system for low H coverage. Since the clean Si dimers have additional π -bonding, it is energetically more favorable for two H atoms to sit at the same Si dimer than at two different ones. An estimate for the energy gain derived from experiment gives 0.25eV [2], the best theoretical estimate at the moment is about 0.15eV [19]. Due to this effect the hydrogen atoms are “pre-paired” prior to desorption for coverages that are not too low. The desorption rate is therefore proportional to the coverage, rather than the coverage squared, as usually expected for associative desorption. Restricting our further investigation to the desorption from such a “doubly-occupied” Si dimer, our mechanism will be a first order process, in accordance with experimental evidence. We shall first concentrate on the minimum energy pathway for desorption, which is highly asymmetric, and then discuss the alternative of a symmetric pathway.

3.2 Desorption pathways

Fig. 1 shows the calculated transition state and minimum energy path assuming that the substrate relaxes completely during each step of the reaction (i.e. the adiabatic limit of substrate motion). As a first step in desorption from the mono-hydride phase one hydrogen atom moves over to the other side of the Si dimer. Simultaneously the dimer itself changes from a symmetric to a buckled configuration. The two H atoms pass through a highly asymmetric transition state. Finally the H_2 molecule leaves the surface, while the Si dimer buckles even stronger until it has reached its equilibrium configuration on the clean surface. The details of the transition state are given in fig.3(a). Our findings give evidence for a strong coupling of the desorption process to the Si dimer buckling angle, while the Si-Si distance within the dimer at the transition state is almost the same as in the mono-hydride. Since the final step essentially takes place at a single silicon atom, our mechanism fits well into the picture of a common exit channel for H_2 desorption from all silicon surfaces, which has been invoked to explain similar final state distributions for H_2 from different surface orientations and adsorbate phases observed in experiment [10]. We would like to point out, however, that the system never passes through the metastable di-hydride species mentioned above, but follows a direct route from the adiabatic transition state to the mono-hydride, as can be seen from the energy diagram in fig.2.

If we require the mirror symmetry of the mono-hydride phase to be retained during desorption, we arrive at the symmetric transition state shown in fig.3(b).

The breaking of the H_2 bond occurs already with the molecule further out above the surface as compared to the asymmetric pathway. Since it is only 0.08 eV higher in energy than the asymmetric one, contributions to the desorption rate cannot be excluded from simple activation energy arguments. Instead, a more detailed kinetic analysis is needed, which accounts for the different prefactors for each pathway. We have therefore included the symmetric transition state in the following analysis.

The desorption from the Si(100) surface is comparable to H_2 abstraction from disilane, where the Woodward-Hoffmann rules have been invoked to explain why an asymmetric transition state is favored [35]. There are, however, important differences between the reverse processes, the adsorption and the addition of H_2 to disilene. The latter process has a symmetric transition state, and the π -bond in the surface Si dimer is much weaker due to geometrical constraints on the surface, compared to π -bonding in disilene. For both reasons we get a substantially lower adsorption barrier compared to the barrier of 1.65 eV for (symmetric) addition of H_2 to disilene [35].

3.3 Coupling to the substrate

Because of the strong coupling of the dimer motion to desorption we also expect a strong dependence of the barrier for sticking on the substrate configuration. There is, however, an important difference between sticking and desorption. In a thermal desorption experiment, the system probes a large part of the multi-dimensional potential energy surface before it (most likely) finds its way over the lowest transition state. This situation should adequately be described by a kinetic theory including all relevant degrees of freedom. In an adsorption experiment, the molecule will either overcome the barrier towards sticking or immediately be reflected to the gas phase. In a first approximation, we can assume that each H_2 molecule probes a single frozen substrate configuration in its encounter with the surface. Most of these configurations will exhibit a large adsorption barrier, but sometimes a thermal fluctuation of the surface will create a configuration favorable for sticking. The observed sticking could be completely determined by these thermally activated events. Such a scenario has been proposed to resolve the apparent contradiction between desorption and sticking experiments [12, 36].

In this context the question arises which modes of the silicon dimer are the most important ones for such an activated sticking. Fig. 1 clearly shows that the lower Si atom of the dimer changes its position, while the upper one moves only little. Apart from a minor change in the Si dimer bond length, this motion can be described as a change of the buckling angle. We therefore investigated the influence of the buckling on the asymmetric transition state. Additionally, we have studied the importance of the Si dimer stretch mode for the symmetric transition state.

To order to explore the coupling between the H_2 molecule and the Si dimer buckling in more detail, we tried to place H_2 in a transition state geometry asymmetrically on both a fully buckled dimer and a symmetric dimer. In fig. 6 the total energies

$E_{TS}(x)$ of these configurations (relative to the equilibrium surface energy plus the energy of the free molecule) are shown as a function of buckling angle x . The lower curve, $E_s(x)$, displays the energy of the corresponding Si dimer configuration on the clean surface. Its minimum is the result of a balance between two effects: The buckling increases the splitting between the bonding and antibonding state derived from the two dangling bonds in the Si dimer, until a gap opens and the surface becomes semiconducting. On the other hand, it introduces additional surface strain, which limits the favorable amount of buckling.

Within the simple static picture outlined above, we can introduce the difference $E_a(x) = E_{TS}(x) - E_s(x)$ as the barrier height felt by a molecule hitting a surface frozen in that particular configuration. Alternatively, it can be interpreted as the energy gained by a desorbing molecule after traversing a saddle point with the substrate coordinates held fixed.

A similar analysis for the coupling to the stretch mode of the symmetric Si dimer is made in fig.7. We continuously weakened the Si dimer bond by enforcing a fixed distance y in the Si dimer and determined the symmetric transition state for each of these configurations. For a reasonable Si dimer stretch we find only minor changes in the static barrier $E_a(y)$. Only for the unrelaxed, unpaired Si(100) surface this barrier decreases to 0.15eV. Although unpaired silicon atoms occur only very rarely on a well-prepared Si(100) surface, this result indicates that the barrier for sticking can become unusually low in this situation. We expect a similar conclusion to hold for single atom defects.

We also tested the stability of the symmetric transition state against buckling of the Si dimer (dashed line in fig. 6). With increasing buckling the most favorable transition state is seen to move over from the symmetric configuration to the lower silicon atom of the dimer. To explain this tendency it is beneficial to consider the energetics of adsorption as governed by a balance between repulsive effects from the filled orbitals of the adsorbing molecule and attraction caused by hybridization of the molecule's antibonding states with the electronic states of the substrate [37]. The energy of the dangling bond state of the lower/upper silicon atom is raised/lowered in energy during the buckling [38], which results in electronic charge being transferred from the lower to the upper Si atom. This effect is clearly visible in fig.4. The H_2 molecule can minimize its repulsion with the surface by approaching the depleted lower end of the Si dimer. For that reason, buckling tends to facilitate dissociation. On the symmetric Si dimer, both dangling bonds are occupied with one electron each. Placing the H_2 above one end of the symmetric Si dimer causes repulsion between the electrons in the $1\sigma_g$ state of hydrogen and the electron in the dangling bond state, and is energetically unfavorable (cf. fig. 4 and 6). In this situation, the symmetric pathway is preferred. A discussion of the attractive interaction between the molecule and the surface partially counterbalances the above trends. As can be seen from fig.5, the splitting of the bonding and antibonding surface states is increased by the interaction with the H_2 molecule during adsorption and the antibonding state

is partially removed from the gap. The energy gain is largest when the antibonding state was yet partially occupied before the interaction, i.e. when the buckling was too small to make the clean surface semiconducting. As a result of both the repulsive and the attractive interactions, the lowest adsorption barrier occurs for some intermediate value of the buckling angle.

3.4 The transition states

The observed very low sticking has raised the question of an entropic contribution to the adsorption barrier. To quantify the steric constraints for the reaction, we performed a normal mode analysis for the molecule at both the lowest asymmetric and symmetric transition state. The results are shown in table 2. For the asymmetric transition state, the four degrees of freedom of the molecule moving in the plane of the Si dimer are found to be strongly coupled. The reaction coordinate has components both in the direction of the stretch of the molecular bond and the motion of the molecule’s center of mass parallel to the surface. This reflects the observation that one hydrogen is stripped from the molecule as it passes the lower silicon atom. The frequencies of the real modes are fairly high compared to metallic systems [27, 39, 40], indicating strong configurational constraints for the reaction to take place. This can be rationalized by the covalent character of the bonding on the Si surface, which leads to a strong corrugation of the potential. The sum of all real frequencies, 585 meV, even exceeds the vibrational energy quantum of H_2 .

The symmetric transition state lies further out above the surface. Here the molecule feels a less strongly corrugated potential, which is reflected by the low lying modes associated with the variation of the molecule’s impact position within the unit cell. The mode associated with the bond stretch, however, has only dropped to one half of its gas phase value. Again, the sum of all real modes, 475 meV, is sizeable.

As a consequence, the barrier for adsorption through both the symmetric and the asymmetric transition state depends extremely strongly on the impact parameter in the surface unit cell and the orientation of the incoming molecule. Only a tiny fraction of the molecules that have just enough energy to surmount the minimum energy barrier will actually impact the surface with the right configuration. As the energy of the incoming molecule increases, the "hole" in configuration space where it can get over the barrier will increase, thus leading to a slow rise of the sticking coefficient.

4 Discussion

4.1 Desorption

Combining the obtained information about the potential energy surface of the H_2/Si system with some simple dynamical considerations can shed some new light on the puzzling experimental data.

To check the reliability of our results, we first give an estimate for the activation energy for desorption which includes zero-point energies. We have calculated the vibrational frequencies of the mono-hydride to be 256 meV for the Si-H stretch (the experimental value is 260 meV, see ref. [41]) and 77 meV for each of the bending modes. Including all zero-point energies at the transition state, we get a desorption energy of 2.50 eV (see fig. 2), in excellent agreement with the most reliable experimental values [2, 8, 9].

We can also account for the observed vibrational excitation of the desorbing molecules. At the calculated transition state the H-H bond is stretched by 35% and the associated frequency is lowered (see fig. 8). Together with the potential drop after the barrier this will give rise to molecules desorbing vibrationally excited [42], in qualitative agreement with the observations [10].

To comment on the energy in the other degrees of freedom of the molecule a more careful dynamical treatment is needed. Because of the confined transition state and stiff normal modes, transition state theory would predict that a sizeable amount of zero point energy should end up as kinetic energy of the molecule. As mentioned earlier, the sum of the normal mode energies is of the order of the H_2 vibrational quantum for both transition states we have examined, and therefore the *total* excess energy of the desorbing molecules is essentially given by $E_a(x)$ in this model. However, transition state theory may not be applicable, because desorption is too fast to establish thermal equilibrium at the transition state, and only a fraction of the zero point energy will actually contribute to the final energy of H_2 . Because of the strong mixing of the molecular modes at the transition state the detailed energy distribution among the vibrational, rotational and translational degrees of freedom will have to await quite elaborate calculations of the desorption dynamics.

It should be mentioned that the surface phonons will also take up part of the energy released after passing the desorption barrier. Since the surface atoms are considerably heavier than hydrogen, it is a reasonable first approximation to assume that they will stay in the saddle point configuration during desorption. In this limit the energy released to the substrate coordinates can be read from the $E_s(x)$ curve in fig.6 and amounts to 0.09 eV for the most favorable configuration. In a more realistic treatment, the desorbing H_2 molecule will transfer momentum to the substrate, thereby causing the Si dimer atoms to recoil. We therefore expect the above number to be a lower limit for the energy transfer to phonons. A detailed investigation of this effects is currently in progress [43].

Nevertheless, our calculations suggest that a sizeable amount of energy, up to 0.4 eV, depending on the desorption pathway, the exact barrier height and the role of

zero point energy, will end up in the molecular degrees of freedom. Experimentally, it has been found that the molecules have $0.077 \pm 0.08\text{eV}$ in excess of their thermal energy after desorption [12]. Although a quantitative comparison of theory and experiment will have to await a full dynamical treatment, this finding seems to indicate that our GGA calculation overestimates the barrier slightly. We tried different slab geometries and basis-set sizes and found an uncertainty in the barrier height of the order of 0.1eV (see table 1). Further sources of systematic errors could be the interaction between hydrogen in different unit cells and the non-selfconsistent treatment of the GGA corrections in our approach, and last, but not least the GGA itself. Indeed, similar calculation using a larger unit cell have reported a somewhat lower barrier height [21].

4.2 Adsorption

The apparent absence of sticking on the cold clean surface is readily explained by the static barrier height of 0.67eV together with the strong steric constraints on the transition state we have found. Heating the surface will excite the Si dimer to a less buckled configuration with a lower barrier and thus promote sticking. Both effects have been demonstrated in a simple dynamical model, which treats the slow degrees of freedom in a classical sudden approximation [20]. The modulation of the barrier height with buckling angle results in a sticking coefficient increasing with surface temperature with an apparent activation energy of 0.09 eV for beam energies up to about 0.3 eV , and slightly lower at higher energies. A more elaborate treatment of the dynamics, taking into account two molecular and one substrate degree of freedom, gave similar results [44]. As has been pointed out before [20], this activation energy can simply be interpreted as the energy $E_s(x_m)$ required to bring the clean surface Si dimer to the angle x_m where $E_a(x)$ has its minimum. At low kinetic energies the adsorption process is therefore dominated by the minimum barrier $E_a(x_m)$, and the rate is directly proportional to the probability that a thermal fluctuation brings the surface in a configuration of a lower barrier for the reaction. In a realistic model of sticking, the dynamical coupling between the impinging molecule and the substrate has to be taken into account as well. Although such a coupling seems to be suppressed by the large mass mismatch between hydrogen and silicon, it will certainly effect the sticking probability for incident energies substantially lower than the barrier height, when tunneling is important. The so-called “thermally assisted tunneling” can give rise to a strong increase of the sticking coefficient with surface temperature, and when being interpreted as an apparent activation energy, its value will vary strongly with the incident energy of the molecules [45]. The implications of this coupling for the sticking of D_2 on $\text{Si}(100)$ are currently being investigated [43].

The angular dependence of the sticking has not been measured yet. From the normal mode analysis of this transition state we find that the reaction coordinate couples strongly to the motion of the molecule parallel to the surface. We therefore

conclude that parallel momentum is probably important in accessing the transition state. Hence we expect the sticking probabilities not to obey normal energy scaling as a function of incident angle.

5 Conclusion

In conclusion, we have shown that *ab initio* calculations give evidence for a decisive role of surface structure in the interaction of H_2 with the Si(100) surface. We find a direct desorption pathway from the mono-hydride phase in accordance with the observed activation energy. Combined with the pre-pairing mechanism, this also explains the peculiarities of reaction order on this surface. Adsorption is strongly hindered both by a sizeable static barrier and a strongly confined transition state. Both the barrier height and location couple strongly to the surface modes, and we find a buckling mode of the silicon dimer to promote the sticking very efficiently.

Finally, we would like to point out that this is the rationale behind both the phonon-assisted sticking and the apparent lack of “detailed balance” in the experiments. Although we find a unique lowest transition state, adsorption and desorption experiments are not reciprocal to each other, as is usually assumed in the application of “detailed balance” arguments, since the initial and final configurations of the silicon dimer are different in both adsorption and desorption (actually they are interchanged). As a consequence, adsorption and desorption experiments reveal different aspects of the H_2 /Si(100) interaction potential.

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surface cell	E_c [Ryd]	N_l	N_k	slab type	$E_a(x)$ [eV]	
					$x = 11.7^0$	$x = 17.4^0$
2x1	30	6	32	s	0.39	0.67
2x1	30	8	32	s	0.38	—
2x1	40	6	32	s	0.46	—
2x1	30	6	32	p	0.31	0.62
2x1	30	6	128	p	0.34	—
c(4x2)	30	6	16	p	0.37	—

Table 1: Convergence test for the adsorption barrier height on a Si dimer tilted by 11.7 and 17.4 degrees, for different sizes of the unit cell, cutoff-energies E_c , numbers of layers in the slab N_l , and k-points in the surface Brillouin zone N_k . On the slabs labeled “s” the adsorption was modeled symmetrically on both sides, for the slabs labeled “p” one side was passivated by fixed hydrogen atoms. The c(4x2) unit cell contained two Si dimers with opposite buckling angles, but the same transition state configuration as in the 2x1 cell was used.

Normal mode	adiab. TS $\hbar\omega$ [meV]	sym. TS $\hbar\omega$ [meV]
Reaction coordinate	<i>i</i> 130	<i>i</i> 190
H–H stretch	180	260
Si–H ₂ stretch	100	–
Hindered cartwheel	165	115
Hindered helicopter	95	80
Translation parallel to dimer	–	15
Translation normal to dimer	45	5
Sum of real modes	585	475

Table 2: The normal modes of the H₂ molecule at the adiabatic and the symmetric transition state. The labels are chosen as a hint to what the mode resembles most closely. The missing entry is the main component of the reaction coordinate.

Figure 1: The calculated minimum energy path for an H_2 molecule dissociating over a Si(100) surface. The trajectories of the H and surface Si atoms are shown and the transition state is marked. The initial, transition, and final state configurations are also indicated as full, dashed and long dashed circles, respectively.

Figure 2: Potential energy for an H_2 molecule approaching the Si(100) surface along the minimum energy reaction path. The full line assumes that the surface dimer is already in the most favorable configuration for sticking before the approach, whereas the dashed line is for the Si dimer fixed in its equilibrium configuration. The levels shown in the plot indicate the zero point energy contributions at the initial, transition and final state.

Figure 3: The geometries of the adiabatic transition state (a) and the symmetric transition state (b).

Figure 4: Charge densities projected onto a plane perpendicular to the clean Si(100) surface which contains the surface Si dimer. From top to bottom the symmetric Si dimer, the most favorable Si dimer configuration for H_2 adsorption, and the equilibrium configuration are shown. The hydrogen molecule will most favorably adsorb on the charge depleted lower end of the Si dimer.

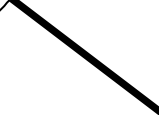
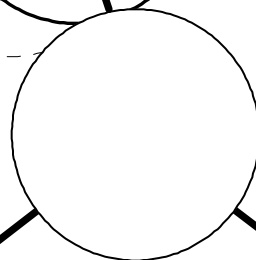
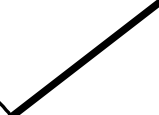
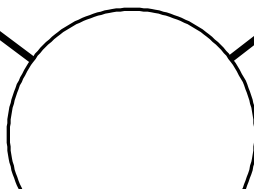
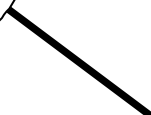
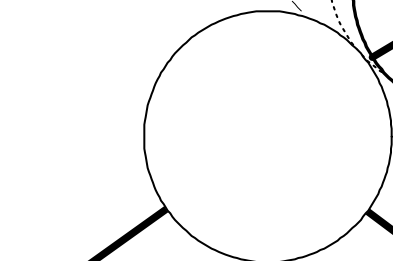
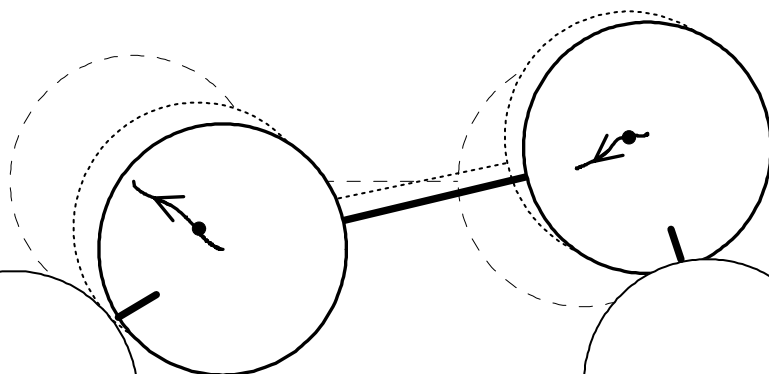
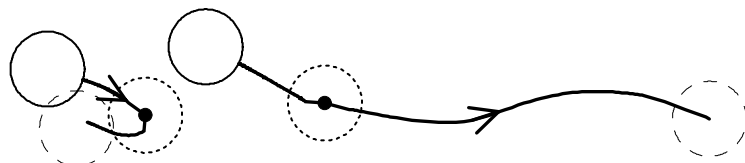
Figure 5: Surface band structure for the Si dimer in its equilibrium configuration (a) and in the configuration of the adiabatic transition state (b). The first two energy levels above and below the Fermi energy (which is set to 0) are shown. Full lines refer to the clean surface and dotted lines to a situation with H_2 present at the transition state. In (b) the surface conduction band becomes depleted upon adsorption. This effect tends to lower the adsorption barrier.

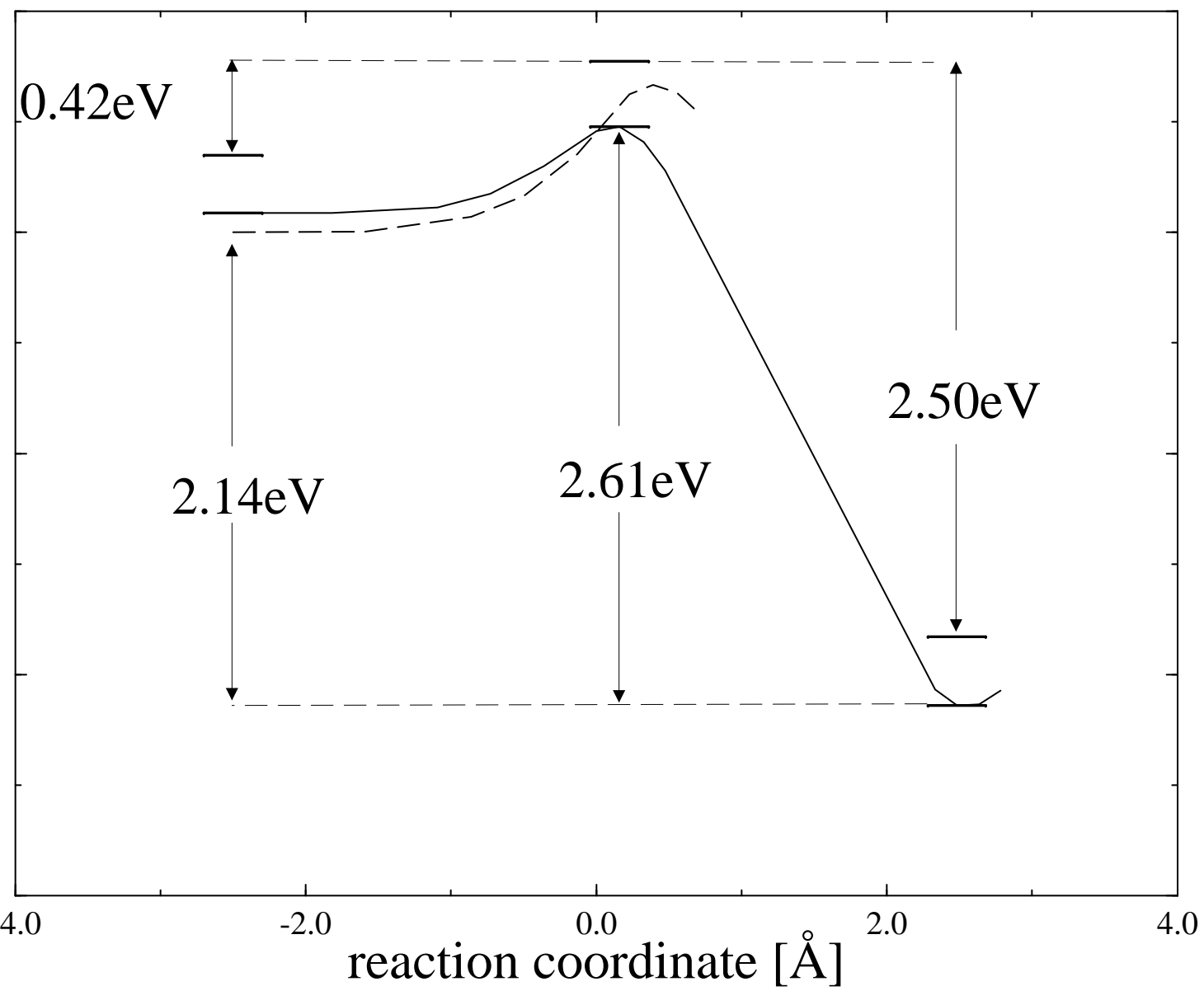
Figure 6: The total energy of the transition state E_{TS} , of the clean surface E_s and the activation barrier for dissociation E_a shown as a function of the buckling angle of the Si surface dimer. While a nearly symmetric transition state is favored for small buckling angle, the asymmetric transition state is preferred at higher buckling angles. The curves are fits based on the data points and the known location of the minima. A second order polynomial in x was used for E_{TS} and a third order polynomial in x^2 for E_s .

Figure 7: The total energy of the symmetric transition state E_{TS} , of the clean surface E_s and the activation barrier for dissociation E_a shown as a function of the Si dimer bond length. The lines are fits to guide the eye. The data points on the very right correspond to the unpaired, unrelaxed Si(100) surface.

Figure 8: Entrance channel of the potential energy surface for an H_2 molecule impinging under 63° relative to the surface normal onto the lower silicon atom of the surface dimer, which is frozen in the position of the lowest barrier. The molecule is oriented with its axis almost parallel to the surface. The center-of-mass distance refers to the midpoint between the two hydrogen atoms in the mono-hydride phase. The energy is given relative to the energy of the frozen surface plus the energy of the free H_2 molecule, the contour spacing being 50 meV.

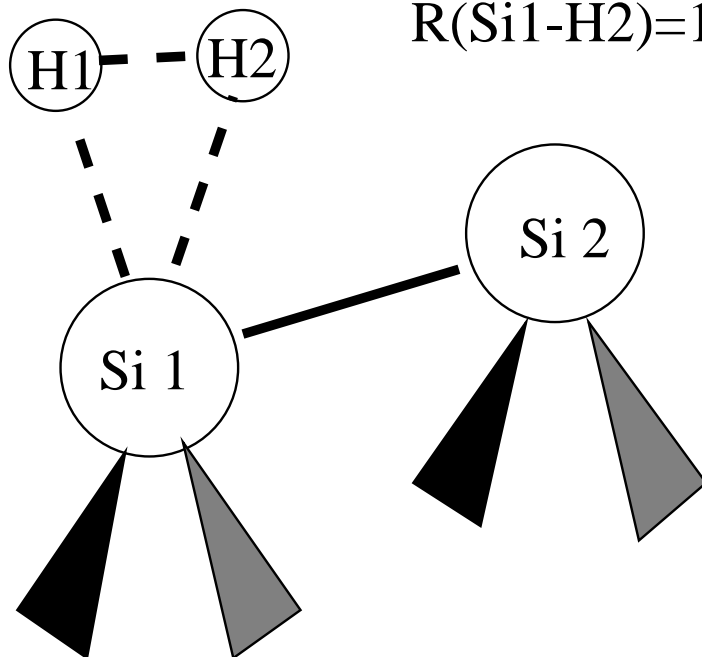
1 Å





(a)

$R(\text{H1-H2})=1.01\text{\AA}$
 $R(\text{Si1-Si2})=2.38\text{\AA}$
 $R(\text{Si1-H1})=1.69\text{\AA}$
 $R(\text{Si1-H2})=1.78\text{\AA}$



(b)

$R(\text{H1-H2})=0.90\text{\AA}$
 $R(\text{Si1-Si2})=2.42\text{\AA}$
 $R(\text{Si1-H1})=2.08\text{\AA}$

